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(54) **New catalyst, process for the production of hydrogen peroxide and its use in oxidation processes**

Neuer Katalysator, Verfahren für die Herstellung von Wasserstoffperoxid und seine Verwendung für Oxidierungsverfahren

Nouveau catalyseur, procédé pour la production de l'eau oxygénée et son utilisation dans les procédés d'oxydation

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(56) References cited:  
**EP-A- 0 542 620 WO-A-99/59915**  
**US-A- 4 661 337 US-A- 5 489 564**  
  
• **PATENT ABSTRACTS OF JAPAN vol. 013, no.**  
**185 (P-865) 02 May 1989 -& JP 01 013 150 A (FUJI**  
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**EP 0 978 316 B1**

## Description

[0001] The present invention relates to a catalyst consisting of a metal of the VIII group supported on acid activated carbon functionalized with sulfonic groups, a process for the direct synthesis of hydrogen peroxide from hydrogen and oxygen which uses said catalyst and the use of the hydrogen peroxide solution in oxidation processes catalyzed by titanium-silicalite.

[0002] Hydrogen peroxide is a commercially important product which is widely used as bleaching agent in the textile and paper industries, in the environmental field as a biocide and in the chemical industry.

[0003] In particular the use of hydrogen peroxide is known in the art in a series of oxidation reactions catalyzed by titanium silicalite, such as for example the epoxidation of olefins (EP-100.119, the ammoximation of carbonyl compounds (US 4.794.198), the oxidation of ammonia to hydroxylamine (US 5.320.819) and the hydroxylation of aromatic hydrocarbons (US 4.369.783).

[0004] Generally solutions of hydrogen peroxide are used, obtained by synthesis processes which are based on the alternating oxidation and reduction of alkylanthraquinones.

[0005] These processes however, have substantial disadvantages deriving from the necessity of operating with large volumes of reagents, the numerous steps required, the relatively high cost of the intermediates and the production of inactive by-products.

[0006] As a result, other processes for the synthesis of hydrogen peroxide have been proposed in the art, among which those using a catalytic system consisting of a noble metal, preferably palladium, supported on a carrier, for the direct synthesis of hydrogen peroxide from hydrogen and oxygen.

[0007] For example, U.S. patent 4.772.458 describes a process for the synthesis of hydrogen peroxide which uses a catalyst based on palladium supported on coal, in which the reaction is carried out in water in the presence of hydrogen ions and bromide ions in a molar ratio of at least 2:1.

[0008] The  $H^+$  and  $Br^-$  ions are supplied as a combination of a strong acid such as sulfuric, phosphoric, hydrochloric or nitric acid, and a bromine salt.

[0009] Quantities of acid ranging from 2.5 to 10 g/litre are generally required to obtain high concentrations of  $H_2O_2$ .

[0010] The use of high quantities of acid, in addition to creating problems of a technological nature, for example corrosion of the autoclaves, also causes serious problems relating to the dissolution of the active phase (metal) of the catalyst in the reaction medium, with a consequent reduction in the activity and life of the catalyst itself.

[0011] The metal dissolved in the reaction medium, moreover, is difficult to recover with the recycling methods at present available.

[0012] In addition, the process operates under critical conditions as concentrations of  $H_2 > 5\%$  (generally 18%) with respect to the reaction mixture, are used, which is therefore within the explosivity limits of  $H_2/O_2$  mixtures.

[0013] U.S. patent 4.889.705 relates to an improved process for the synthesis of hydrogen peroxide in which the  $H^+$  and  $Br^-$  ions are supplied directly as  $HBr$ . Operating according to this process quantities of  $Br^-$  ions of more than  $10^{-4}$  moles/litre are required to obtain hydrogen peroxide. The use of high quantities of halides creates problems of instability of both the catalyst metal and the hydrogen peroxide solution produced.

[0014] To overcome these drawbacks alternative processes have been proposed which can be carried out without acids and/or bromine ions in the reaction medium.

[0015] For example, patent application EP-492.064 describes a process for the synthesis of hydrogen peroxide from hydrogen and oxygen, which uses a catalyst based on palladium supported on a halogenated resin, in particular a brominated styrene/divinylbenzene resin.

[0016] The reaction is carried out in water, in the presence of an acid selected from sulfuric, phosphoric or nitric acid. Operating with this process however, concentrations of  $H_2O_2$  of about 0.58% are obtained.

[0017] EP-504741 describes a process for the synthesis of  $H_2O_2$  from hydrogen and oxygen which uses a catalyst based on palladium or platinum supported on an acid or superacid carrier selected from molybdenum, zirconium or tungsten oxides.

[0018] The reaction is carried out in water, in the presence of a promoter selected from bromine salts in quantities of more than 0.1 mmol/l of reaction mixture. Operating according to this process hydrogen peroxide is obtained in concentrations not higher than 1%.

[0019] U.S. patent 5.320.921 describes a process for the synthesis of  $H_2O_2$  from hydrogen and oxygen which uses a catalyst based on palladium or platinum supported on a heteropolyacid made insoluble in water. The reaction is carried out in water in the presence of bromine ions (0.5 mmol/litre of sodium bromide). Quantities of  $H_2O_2$  equal to about 1.1% are obtained.

[0020] These processes of the known art, therefore, do not have a productivity, referring to the quantity of hydrogen peroxide produced, which is sufficiently high for their application on an industrial scale to be of interest.

[0021] There is consequently an evident necessity for further improvements in the field of the production of hydrogen peroxide.

[0022] It has now been found that it is possible to satisfy these demands of the known art by means of a simple and convenient process which is based on the use of a catalyst consisting of a metal of group VIII supported on acid activated carbon functionalized with sulfonic groups.

[0023] The use of functionalized activated carbon containing the acid function directly bound to the surface and not released in the reaction medium has significant advantages, in particular:

- (i) the possibility of using extremely low quantities of halides ( $< 10^{-4}$  moles/litre) ;
- (ii) the possibility of operating without free acids or in the presence of traces of free acids ( $H^+ < 10^{-4}$  moles/l) ;
- (iii) the production of a stable catalyst; the quantity of noble metal in solution is less than 3 parts per billion (ppb);
- (iv) the production of stable solutions of hydrogen peroxide;
- (v) the production of solutions of hydrogen peroxide in high concentrations.

[0024] This is an advantage for subsequent uses of  $H_2O_2$  in oxidation processes, as intermediate processing operations such as, for example, the removal of solvents, are not required. In particular, the concentration of hydrogen peroxide which can be obtained with the process of the present invention is highly compatible with a direct use in oxidation reactions catalyzed by titanium-silicalite, without requiring concentration steps.

[0025] The presence of only traces of halides and acidity is not a disadvantage for direct use in the above reactions, as the possible introduction of salts or acidity in downstream processes is minimized.

[0026] In accordance with this, a first aspect of the present invention relates to a catalyst consisting of a metal of group VIII supported on an acid activated carbon functionalized with sulfonic groups.

[0027] A further object of the present invention relates to a method for the preparation of an activated carbon functionalized with sulfonic groups.

[0028] The present invention also relates to an activated carbon functionalized with sulfonic groups and its use as a carrier for catalysts based on metals.

[0029] Yet another object of the present invention relates to a process for the production of hydrogen peroxide starting from hydrogen and oxygen, in a solvent, in the presence of a promoter and a catalytic system consisting of a metal of group VIII supported on a carrier, characterized in that said carrier is an activated carbon functionalized with sulfonic groups.

[0030] The present invention additionally relates to the use of solutions of hydrogen peroxide obtained as described above in an oxidation process catalyzed by titanium-silicalite.

[0031] Further objects of the present invention are evident in the following description and claims.

[0032] Examples of activated carbon which can be used for the purposes of the present invention can be selected from activated carbon available on the market with a surface area of at least  $100 \text{ m}^2/\text{g}$ .

[0033] Activated carbon with a surface area higher than  $300 \text{ m}^2/\text{g}$  is preferably used.

[0034] The activated carbon used can be in the form of powder, granules, pellets, etc.

[0035] The activated carbon can be used as such or it is pretreated by washing with a diluted solution, generally between 1 and 10% by weight, of aqueous hydrochloric acid, at  $50-80^\circ\text{C}$ .

[0036] The functionalization is carried out with a sulfonating agent preferably selected from sulfuric acid,  $\text{SO}_3$  or oleum.

[0037] The functionalization of activated carbon is generally carried out using a weight ratio sulfonating agent:activated carbon ranging from 1:20 to 20:1, preferably between 1:5 and 5:1.

[0038] The functionalization reaction is carried out at a temperature ranging from  $50^\circ\text{C}$  to  $350^\circ\text{C}$ , preferably from  $70^\circ\text{C}$  to  $200^\circ\text{C}$ , for a period of time selected in relation to the temperature and sulfonating agent.

[0039] The activated carbon thus treated is then washed with water until neutrality of the washing water. The functionalized activated carbon is subsequently treated with an oxidizing agent. A diluted aqueous solution of  $H_2O_2$  (1-4% by weight) is preferably used, with a weight ratio sulfonated carbon: $H_2O_2$  solution ranging from 1:10 to 1:100, preferably between 1:20 and 1:50.

[0040] The resulting suspension is maintained, under stirring, at a temperature ranging from  $30$  to  $100^\circ\text{C}$ , preferably from  $50$  to  $70^\circ\text{C}$ , for a period of time ranging from 1 to 4 hours. It is then filtered, washed until the disappearance of the oxidizing agent in the washing water and is then dried at a temperature ranging from  $100^\circ\text{C}$  to  $120^\circ\text{C}$ .

[0041] The characterization of the functionalized activated carbon by means of photoelectron spectroscopy (XPS) reveals the presence of a peak characteristic of  $\text{C-SO}_3\text{H}$  groups.

[0042] This method is capable of providing information on the chemical species present on the surface of a solid sample (within  $5 \text{ nm}$  approx.), on the oxidation states of a certain element, and also on the ligands of a particular atom, in fact the position of the signal is determined by the electronic exchange with the environment.

[0043] The sensitivity limit for sulfur can be estimated at about 50 ppm in the volume analyzed ( $1257 \text{ microns}^2 \times 5 \text{ nm}$ ). The analysis is carried out in ultra high vacuum (UHV) ( $10^{-10}$  Torr) and consequently the species physisorbed on the surface are eliminated and the essentially chemically bound species are analyzed.

[0044] As the samples are good electric conductors, the analysis is not affected by problems of surface electrostatic charge. The peak positions recorded on the axis of the "Binding Energies" are therefore not influenced by error, as they have been calibrated with an appropriate internal standard.

[0045] Semi-quantitative analysis (atomic %) provides the atomic concentrations of all the elements present above the sensitivity limit except for hydrogen which cannot be determined.

[0046] High resolution analysis of the sulfur signal (S) gives indications on the relative chemical environment.

[0047] Figures 1 and 2 show the enlarged peak of sulfur alone. It can be observed that the sulfur of the sample of sulfonated activated carbon is symmetrical with an enlargement of about 3 eV (Binding energy); this indicates the presence of a univocal but energetically heterogeneous species on the surface. The position in energy of the peak maximum ( $168.4 \pm 0.2$  eV), compared with the data supplied by the reference handbook (Handbook of XPS, ed J. Chastain, PE Corporation, MO USA, 1992, pages 60-61) unequivocally indicates the presence of a sulfur species of the sulfonic type ( $-\text{SO}_2\text{OH}$ ) which is expected between 167-169 eV. This species cannot be confused with sulfur of the sulfide type (161-163 eV), or with sulfur of the sulfate type (169-171 eV).

[0048] Operating as described in the experimental examples below, functionalized activated carbon is obtained with a sulfur content of 0.3 to 0.5% by weight with respect to the carrier.

[0049] However, lower or higher quantities than these values can be introduced depending on the starting carrier and operating conditions.

[0050] Quantities of sulfur ranging from 0.1 to 1.0% by weight are sufficient for the purposes of the present invention.

[0051] The catalyst of the present invention is prepared by supporting a metal of group VIII on activated carbon functionalized as described above.

[0052] Non-limiting examples of metals of group VIII are selected from palladium, platinum, ruthenium, iridium, rhodium or combinations of these. Palladium or platinum are preferably used. Palladium is particularly preferred.

[0053] The quantity of metal supported on functionalized activated carbon is between 0.05 and 5% by weight, preferably between 0.1 and 1% by weight.

[0054] The preparation of the catalyst of the present invention can be carried out by means of impregnation or adsorption of a soluble salt of the metal, optionally followed by a reduction phase of the metal with hydrogen or chemical reducing agents, according to the conventional techniques.

[0055] Metal salts selected from acetates, halides and oxalates are preferably used.

[0056] The catalyst of the present invention is particularly advantageous in a process for the direct preparation of hydrogen peroxide from hydrogen and oxygen in a solvent in the presence of a promoter selected from halogenated compounds.

[0057] The catalyst is used in catalytic quantities generally ranging from  $10^{-6}$  to  $10^{-2}$  moles of metal contained in the catalyst per litre of reaction medium.

[0058] Advantageous results are obtained using quantities of catalyst ranging from  $10^{-4}$  to  $10^{-3}$  moles of metal contained in the catalyst per litre of reaction medium.

[0059] The reaction solvent is selected from water, alcohols, or mixtures of these.

[0060] Examples of alcohols are methyl, ethyl, isopropyl alcohol. Methyl alcohol is preferred.

[0061] A mixture of water:alcohol with a weight ratio ranging from 99/1 to 1/99, preferably between 90/10 and 5/95 is preferably used.

[0062] Examples of promoters are selected from compounds of bromine such as hydrobromic acid, sodium bromide, potassium bromide, sodium bromate or ammonium bromide or compounds of chlorine such as sodium chloride, potassium chloride, ammonium chloride.

[0063] Compounds of bromine are preferred for the purposes of the present invention. Particularly preferred are hydrobromic acid, sodium bromide and potassium bromide.

[0064] A quantity of promoter is normally used which is such as to give a concentration of halide ion of more than  $10^{-7}$  moles per litre of reaction medium, preferably a concentration ranging from  $10^{-6}$  to  $10^{-4}$  moles per litre of reaction medium.

[0065] The production of hydrogen peroxide is effected by reacting oxygen and hydrogen in the reaction medium in the presence of the catalyst and promoter and with or without an inert gas (for example nitrogen), generally at a total pressure higher than atmospheric pressure and preferably between 50 and 300 atmospheres.

[0066] The molar ratio  $\text{H}_2/\text{O}_2$  is between 1/1 and 1/100, preferably between 1/5 and 1/50 and the concentration of hydrogen in the gaseous phase in contact with the liquid reaction medium is conveniently maintained at a value of less than 4.5% molar with respect to the reaction mixture, outside the explosivity limits of the  $\text{H}_2/\text{O}_2$  mixture.

[0067] According to an embodiment of the present invention, the reaction can be carried out using air instead of pure oxygen.

[0068] The reaction is typically carried out at temperatures ranging from  $0^\circ\text{C}$  to  $90^\circ\text{C}$ , preferably between  $15^\circ\text{C}$  and  $50^\circ\text{C}$ .

[0069] At the end of the reaction, the solution containing hydrogen peroxide is recovered and the catalyst is separated and recovered by filtration and recycled to the subsequent reaction.

[0070] The process of the present invention can be carried out in batch or in continuous according to the conventional techniques.

[0071] The resulting solution of hydrogen peroxide can be used as such. However, if necessary it can be subjected to concentration operations to remove the solvent by distillation.

[0072] The process of the present invention enables the reagents to be transformed into  $H_2O_2$  with high conversions and selectivities, obtaining solution of  $H_2O_2$  without acidity or containing only traces of acidity and salts.

[0073] The solutions of hydrogen peroxide thus obtained can be used directly in oxidation processes which involve the use of  $H_2O_2$  without complex intermediate processing operations such as the removal of acids and solvents.

[0074] In particular, the hydrogen peroxide solutions obtained with the process of the present invention can be used directly in oxidation processes catalyzed by titanium silicalite as described in the patents cited above, as they are highly compatible with the optimum reaction conditions in which these processes are carried out with respect to:

- the concentration of  $H_2O_2$  in the solution;
- the absence of acidity or the presence of only traces of acidity or salts;
- the composition of the solvent medium consisting of water, alcohols or their mixtures in a wide range of ratios.

[0075] The use of hydrogen peroxide solutions in oxidation processes comprises the following steps:

(a) preparing hydrogen peroxide by the reaction of hydrogen and oxygen in a solvent containing a promoter, in the presence of a catalyst consisting of a metal of group VIII supported on acid activated carbon functionalized with sulfonic groups;

(b) recovering the reaction mixture containing hydrogen peroxide;

(c) putting the reaction mixture containing  $H_2O_2$  in contact with a substrate selected from olefins, aromatic hydrocarbons, ammonia and carbonyl compounds, in the presence of a catalyst based on titanium-silicalite to obtain the desired oxidated product;

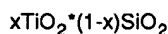
(d) recovering the oxidated product from the reaction mixture of step c); and

(e) recycling the possible non-reacted substrate in step c) and the reaction solvent in steps a) and c).

[0076] Examples of titanium-silicalites which can be used for the purposes of the present invention can be selected from titanium-silicalites with an MFI structure described in the U.S. patent 4.410.501, or the same titanium-silicalites modified with trivalent metals such as, for example, aluminum, iron, boron or gallium. The latter are described in European patents 226.257, 226.258 and 266.825.

[0077] Titanium-silicalites with an MEL or intermediate MFI/MEL structure described in Belgian patent 1.001.038, can also be used.

[0078] The preferred catalyst according to the present invention is titanium-silicalite having the formula:



wherein x represents a number between 0.0001 and 0.04.

[0079] The above titanium silicalites can be prepared according to the method described in the U.S. patent 4.410.501 in which their structural characteristics are also specified.

[0080] The quantity of catalyst used as well as the reaction conditions are selected in relation to the substrate to be oxidated.

[0081] In particular, the epoxidation of olefins can be carried out as described in the patent EP-100.119. The use of a hydro-alcoholic solution of hydrogen peroxide obtained with the process of the present invention advantageously allows in the epoxidation of olefins an improvement in the selectivity, at the same time simplifying the process operations owing to the substantial absence of acidity and/or salts which, in high concentrations, interfere with epoxidation reactions. In fact, a solution of hydrogen peroxide is obtained with only traces of acidity (pH about 4-6, higher than that of commercial hydrogen peroxide) and without stabilizers.

[0082] In the case of an ammoxymation process, (cyclohexanoneoxime from cyclohexanone,  $H_2O_2$ , ammonia), the use of a methanol solution of hydrogen peroxide, instead of tertbutanol (TBA), allows a simplification in the separation section of cyclohexanoneoxime and recycling of the solvent (methanol) as, unlike TEA, it does not form an azeotropic mixture with water.

[0083] The following examples, whose purpose is to describe the present invention in better detail, should in no way be interpreted as limiting the scope of the invention itself.

**EXAMPLE 1****Functionalization of carbon**

**[0084]** 20 g of activated maritime pinewood carbon in powder form (CECA) are charged into a 1 litre glass flask containing 600 ml of an aqueous solution of HCl at 5% by weight. The stirred suspension is brought to 80°C and maintained at this temperature for 2.5 hours. After cooling to room temperature (20-25°C), the suspension is filtered and the carbon recovered is washed with distilled water until elimination of the chlorides and dried in an oven at 120°C for 2 hours.

**[0085]** The activated carbon is charged into a 250 ml glass flask and 40 ml of H<sub>2</sub>SO<sub>4</sub> at 96% are slowly added (in about 2-3 minutes). The carbon-acid mixture is homogenized and then heated in an oil bath to 120°C for 8 hours. At the end of the reaction, it is cooled to room temperature and the activated carbon thus treated is slowly poured into a 1 litre glass containing 500 ml of distilled water. The carbon is then recovered by filtration and washed with distilled water until neutrality of the washing water.

**[0086]** The activated carbon thus treated is suspended in 150 ml of an aqueous solution of H<sub>2</sub>O<sub>2</sub> (3.5% by weight) and the resulting suspension is maintained, under stirring, at 70°C for 2 hours. It is then filtered and washed until the disappearance of H<sub>2</sub>O<sub>2</sub> in the washing water. The sulfonated activated carbon is recovered and dried in an oven at 120°C for 2 hours.

**[0087]** Characterization by means of X-ray induced photoelectron spectroscopy (XPS) shows the presence of a peak relating to the signal C-SO<sub>3</sub>H (figure 1).

**[0088]** The results expressed in atomic % from XPS analysis are indicated in table 1.

Table 1

Sample	C	O	S	Cl	Si	Na
1	88.7%	10.7%	0.12%	0.3%	0.1%	0.06%

**[0089]** Elemental characterization was carried out on the sample of sulfonated carbon (Nr. 1). The results, expressed in mg/kg, are indicated in table 3 and show a sulfur content of 0.39% by weight.

**EXAMPLE 2****Functionalization of carbon**

**[0090]** The same procedure is adopted as in example 1, but carrying out the sulfonation reaction at a temperature of 140°C for 4 hours.

**[0091]** Characterization by means of X-ray induced photoelectron spectroscopy (XPS) shows the presence of a peak relating to the signal C-SO<sub>3</sub>H (figure 2)

**[0092]** The results expressed in atomic % from XPS analysis are indicated in table 2.

Table 2

Sample	C	O	S	Cl	Si	Na
2	90.3%	9.1%	0.14%	0.3%	0.1%	0.08%

**[0093]** Elemental characterization was carried out on the sample of sulfonated carbon (Nr. 2). The results, expressed in mg/kg, are indicated in table 3 and show a sulfur content of 0.48% by weight.

**EXAMPLE 3****Preparation of the catalyst**

**[0094]** 50 ml of methanol and 4 g of activated carbon prepared as described in example 1 are charged into a 250 ml glass flask.

**[0095]** A solution of palladium acetate in acetone (86 mg palladium acetate 98% Aldrich, in 20 ml of acetone) are added dropwise in 2-3 minutes to the stirred suspension. The solution is concentrated with a rotovapor on a bath at 40-50°C, for 10-20 minutes to remove about 30-50% of the solvent. It is filtered with a pump, washed with water, dried in air and then dried in an oven at 110°C for 2 hours. A catalyst is obtained containing 1% of palladium on functionalized

activated carbon.

#### EXAMPLE 4

##### 5 Preparation of the catalyst

[0096] The same procedure is adopted as in example 3, but using 4 g of activated carbon prepared as described in example 2. A catalyst is obtained containing 1% of Palladium on functionalized activated carbon.

##### 10 EXAMPLE 5 (comparative)

[0097] A catalyst is prepared as described in example 3, but using a non-sulfonated activated maritime pinewood carbon in powder form (CECA).

##### 15 EXAMPLE 6

##### Preparation of hydrogen peroxide

20 [0098] 23 mg of catalyst prepared as described in example 4 ( $2 \cdot 10^{-6}$  moles of Pd) and 9 g of a solution of water: methanol (weight ratio 1:8), containing 6 ppm of HBr ( $6 \cdot 10^{-5}$  moles Br/litre reaction mixture) are charged into a 100 ml AISI 316 stainless steel autoclave, equipped with a cylindrical glass container, teflon magnetic stirrer, manometer and heat-exchange apparatus.

[0099] The autoclave is thermostat-regulated at 30°C, closed and then charged with a mixture of gases, previously prepared, consisting of 4% volume  $H_2$ , 4% volume  $O_2$  and 92% volume  $N_2$ , at a total pressure of 65 atm. Stirring is carried out at 900 revs/minute for 1 hour substituting the gas phase every 15 minutes with a mixture of gases having the above composition.

[0100] The autoclave is then depressurized, the content is filtered to remove the catalyst and an aliquot of the solution is analyzed by titration with potassium permanganate to determine the concentration of hydrogen peroxide, which proves to be equal to 2.9% by weight with respect to the reaction mixture.

30 [0101] From the increase in weight of the solution and concentration of  $H_2O_2$ , the selectivity with respect to the converted hydrogen is 50%.

#### EXAMPLE 7

##### 35 Synthesis of hydrogen peroxide

[0102] The reaction is carried out under the same operating conditions indicated in example 6, but using 23 mg of catalyst prepared as described in example 4. A solution is obtained, containing 3.1% by weight of hydrogen peroxide. From the increase in weight of the solution, the selectivity with respect to the converted hydrogen is 58%.

##### 40 EXAMPLE 8 (comparative)

[0103] The reaction is carried out under the same operating conditions indicated in example 6, but using 23 mg of catalyst prepared as described in example 5. A solution is obtained with a content by weight of hydrogen peroxide equal to 0.25%. The selectivity with respect to the converted hydrogen is 7%.

#### EXAMPLE 9

##### Preparation in continuous of hydrogen peroxide

50 [0104] The experimentation is carried out in a 300 ml Hastelloy C steel autoclave, equipped with a magnetic stirrer capable of maintaining the number of revs/minute during the test from 0 to 2000, a pressure controller, a thermostatic jacket and gas-flow controllers.

[0105] 0.45 g of catalyst prepared as described in example 4 ( $4.2 \cdot 10^{-5}$  moles of Pd) and 150 g of water containing 4 ppm of HBr ( $5 \cdot 10^{-5}$  moles of Br/litre of reaction mixture) are charged into this autoclave.

55 [0106] The autoclave is pressurized, without stirring, to 100 atm with a gaseous mixture consisting of 3.6% volume  $H_2$ , 46.4% volume  $O_2$  and 50% volume  $N_2$ . The stirring is then activated up to 1400 revs/minute and the pressure is maintained at 100 atm with a gas flow in continuous equal to 300 l/hour.

[0107] The reaction is followed by gaschromatographic analysis of aliquots of the gaseous phase leaving the reactor every 15 minutes.

[0108] During the test, the conversion of hydrogen is maintained constant (45%).

5 [0109] After 4 hours of reaction at 18°C, the concentration of  $\text{H}_2\text{O}_2$  is equal to 12.5% by weight. The selectivity with respect to the converted hydrogen is equal to 60%.

[0110] The content of  $\text{SO}_4^{2-}$  ion in solution is equal to 3 ppm.

#### EXAMPLE 10

10 [0111] The same procedure is adopted as in example 9, but using as reaction medium 150 g of a mixture of water: methanol with a weight ratio 10:90, containing 3 ppm of HBr ( $3 \cdot 10^{-5}$  moles Br/litre of reaction mixture).

[0112] The production of hydrogen peroxide is carried out at 15°C. The conversion of hydrogen remains constant during the test at 80%.

15 [0113] After 2 hours of reaction, the concentration of  $\text{H}_2\text{O}_2$  was equal to 13.1% by weight. The selectivity with respect to the converted hydrogen is 75%.

[0114] The content of  $\text{SO}_4^{2-}$  ion in solution is equal to 2.5 ppm.

#### EXAMPLE 11

20 [0115] A 380 ml Hastelloy C steel autoclave is used, equipped with a magnetic stirrer, a pressure controller, therostatic jacket and gas-flow controllers.

[0116] 0.60 g of catalyst prepared as described in example 3 ( $5.6 \cdot 10^{-5}$  moles of Pd) and 200 g of water containing 5 ppm of HBr ( $6.2 \cdot 10^{-5}$  moles of Br/litre of reaction mixture) are charged into the autoclave.

25 [0117] The autoclave is pressurized, without stirring, to 95 atm with a gaseous mixture consisting of 3.6% volume  $\text{H}_2$ , 36.4% volume  $\text{O}_2$  and 60% volume of  $\text{N}_2$ . The stirring is then activated up to 1400 revs/minute and the pressure is maintained with a flow in continuous of the same gaseous mixture.

[0118] During the test 120 g/hour of an aqueous solution containing 5 ppm of HBr are fed in continuous and volumes of liquid necessary for keeping the level of the autoclave constant, are discharged. The reaction is carried out at 25°C for 8 hours.

30 [0119] The reaction is followed by gaschromatographic analysis of aliquots of the gaseous phase leaving the reactor every 15 minutes and the liquid phase every hour.

[0120] During the test, the conversion of hydrogen is maintained constant at 85%.

[0121] After 4 hours of reaction, the concentration of  $\text{H}_2\text{O}_2$  is equal to 6.5% by weight. The selectivity with respect to the converted hydrogen is equal to 60%. The content of  $\text{SO}_4^{2-}$  ion in solution is equal to 2 ppm.

35 [0122] After 8 hours of reaction the concentration of  $\text{H}_2\text{O}_2$  and the selectivity with respect to the converted hydrogen remain constant at 6.5% and 60% respectively and the content of  $\text{SO}_4^{2-}$  ion in solution is less than 1 ppm.

#### EXAMPLE 12

40 [0123] The same procedure is adopted as in example 11, but using as reaction medium a mixture of water: methanol with a weight ratio of 4:96, a reaction temperature of 20°C and feeding in continuous 200 g/hour of water:methanol mixture.

[0124] The hydrogen conversion is maintained constant during the test at a value equal to 85%.

45 [0125] In the sampling carried out after 4 hours of reaction, the concentration of hydrogen peroxide in solution is equal to 5.8% by weight. This value remains constant for the whole duration of the test which lasts 20 hours. The selectivity with respect to the hydrogen is 84%. The concentration of  $\text{SO}_4^{2-}$  ion in solution after 20 hours is less than 1 ppm.

#### EXAMPLE 13

50 [0126] The same procedure is adopted as in example 12, using the catalyst prepared as in example 4 and prolonging the reaction for 60 hours.

55 [0127] After 60 hours of reaction the hydrogen conversion is maintained constant at a value equal to 88%, the concentration of  $\text{H}_2\text{O}_2$  is maintained at 6.2% by weight and the selectivity with respect to the hydrogen is 86%. The concentration of  $\text{SO}_4^{2-}$  ion in the reaction effluent from the thirtieth hour is zero.



**EXAMPLE 14****Oxidation of propylene**

5 [0128] 5 g of titanium silicalite TS-1 (EniChem, with a content of titanium equal to 2.05% by weight) in 500 g of methanol are suspended in a 1 l reactor equipped with a mechanical stirrer with a gaseous effect and a thermostatic system (internal coil immersed in the reaction solution and external circulation jacket).

[0129] After thermostat-regulating the system at 40°C and pressurizing with propylene at 1.2 atm (constant for the whole duration of the reaction), 266 g of hydrogen peroxide solution at 6.22%, obtained as described in example 13,  
10 are added in continuous at such a rate as to exhaust the addition of the oxidating agent in 15 minutes.

[0130] After this period a sample of reaction solution is taken.

[0131] The residual  $H_2O_2$  is determined iodometrically, whereas the reaction product is quantified by gaschromatography. The results are:

15 conversion  $H_2O_2$  = 96%  
selectivity to propylene oxide = 97%.

**EXAMPLE 15****Ammonoxylation of cyclohexanone**

[0132] 10 g of titanium silicalite TS-1 (EniChem, with a content of titanium equal to 2.05% by weight) in 500 g of a mixture consisting of:

- 25 - methanol 41% by weight  
- water 31% by weight  
- cyclohexanone 20% by weight  
- ammonia 8% by weight

30 are suspended in a 1l reactor equipped with a mechanical stirrer with a gaseous effect and a thermostatic system (internal coil immersed in the reaction solution and external circulation jacket).

[0133] After thermostat-regulating the system at 80°C and pressurizing with helium at 1.5 atm, 67.5 g of the  $H_2O_2$  solution (6.22%) obtained in example 13 are added in continuous in 5 hours.

[0134] After this period a sample of reaction solution is taken.

35 [0135] The residual  $H_2O_2$  is determined iodometrically, whereas the reaction product is quantified by gaschromatography. The results are:

conversion of cyclohexanone = 92.5%  
selectivity to cyclohexanone = 96%.

40 [0136] The conversion of hydrogen peroxide is quantitative.

Table 3

Elements	CECA carbon as such	Carbon # 1	Carbon # 2
B	20	<1	<1
Na	200	17	20
Mg	2,000	47	47
Al	350	60	100
Si(1)	300	400	380
P	1,300	57	64
S(1)	200	3,900	4,800
Cl(1)	100	<100	<100
K	3,800	68	90
Ca	6,800	90	80
Ti	3	<1	<1

Table 3 (continued)

Elements	CECA carbon as such	Carbon # 1	Carbon # 2
Cr	1	<1	<1
Mn	215	4	4
Fe	140	30	17
Co	<1	<1	<1
Ni	<1	<1	<1
Cu	5	2	8
Zn	3	8	3
Rb	8	<1	<1
Sr	17	<1	<1
Nb	<1	<1	<1
Mo	1	2	<1
Pd	<1	<1	<1
Ag	<1	<1	<1
Ba	11	<1	<1
Ta	<1	<1	<1
Hg(2)	0.11	1.3	1.3
Pb	<1	<1	<1
others	<1	<1	<1

## Claims

1. A catalyst which can be used for the direct synthesis of hydrogen peroxide starting from hydrogen and oxygen consisting of a metal belonging to group VIII supported on a carrier wherein said carrier is an activated carbon containing acid functions, being functionalized with sulfonic groups.
2. The catalyst according to claim 1, wherein the metal belonging to group VIII is selected from palladium, platinum, ruthenium, iridium, rhodium or combinations of these.
3. The catalyst according to claim 2, wherein the metal is palladium.
4. The catalyst according to claim 1, wherein the quantity of metal belonging to group VIII is between 0.05 and 5% by weight with respect to the carrier.
5. The catalyst according to claim 4, wherein the quantity of metal belonging to group VIII is between 0.1 and 1% by weight with respect to the carrier.
6. The catalyst according to claim 1, wherein the functionalized activated carbon contains from 0.1 to 1% by weight of sulfur.
7. The catalyst according to claim 1, obtained by a method which comprises:
  - a) putting the activated carbon in contact with a sulfonating agent with a weight ratio sulfonating agent:carbon ranging from 1:20 to 20:1, at a temperature ranging from 50 to 350°C; and
  - b) washing the functionalized activated carbon with water until neutrality of the washing water;
  - c) treating the sulfonated activated carbon obtained in step b) with an oxidating agent, at a temperature ranging from 30 to 100°C;
  - d) washing the functionalized activated carbon obtained in step c) until the disappearance of the oxidating agent in the washing water and drying at a temperature of 100 to 120°C; and finally
  - e) supporting the metal of group VIII on activated carbon functionalized with sulfonic groups.
8. The catalyst according to claim 7, wherein step a) is preceded by a step a') wherein the activated carbon is washed with an aqueous solution of hydrochloric acid 1-10% by weight, at a temperature ranging from 50 to 80°C.

9. The catalyst according to claim 7, wherein in step

a) the weight ratio sulfonating agent:carbon is between 1:5 and 5:1, the temperature varies from 70 to 200°C.

10. The catalyst according to claim 7, wherein the sulfonating agent is selected from sulfuric acid, SO<sub>3</sub> and oleum.

11. The catalyst according to claim 7, wherein in step c) an aqueous solution of hydrogen peroxide is used at a concentration ranging from 1 to 4% by weight, with a weight ratio sulfonated activated carbon and aqueous solution of hydrogen peroxide ranging from 1:10 to 1:100.

12. The catalyst according to claim 11, wherein the weight ratio sulfonated activated carbon and aqueous solution of hydrogen peroxide is between 1:20 and 1:50.

13. The catalyst according to claim 7, wherein in step c) the temperature is between 50 and 70°C.

14. A process for the direct production of hydrogen peroxide by means of the reaction of hydrogen and oxygen in a solvent which contains a promoter in the presence of a catalyst consisting of a metal of group VIII supported on a carrier, wherein said carrier is an activated carbon containing acid functions, being functionalized with sulfonic groups.

15. The process according to claim 14, wherein the metallic catalyst of group VIII is selected from palladium, platinum, ruthenium, iridium, rhodium or combinations of these.

16. The process according to claim 15, wherein the metal is palladium.

17. The process according to claim 14, wherein the promoter is a compound containing a halogen.

18. The process according to claim 17, wherein the compound containing a halogen is selected from the group consisting of hydrobromic acid, sodium bromide, potassium bromide, sodium bromate or ammonium bromide or compounds of chlorine such as sodium chloride, potassium chloride, ammonium chloride.

19. The process according to claim 18, wherein the compound is hydrobromic acid, sodium bromide and potassium bromide.

20. The process according to claim 14, wherein a quantity of promoter is used which is such as to give a concentration of the halide ion of more than 10<sup>-7</sup> moles per litre of reaction medium.

21. The process according to claim 20, wherein a quantity of promoter is used which is such as to give a concentration of the halide ion between 10<sup>-6</sup> and 10<sup>-4</sup> moles per litre of reaction medium.

22. The process according to claim 14, wherein the reaction medium is selected from water, an alcohol or a mixture of these.

23. The process according to claim 22, wherein the alcohol is selected from methanol, ethanol, isopropanol.

24. The process according to claim 23, wherein the alcohol is methanol.

25. The process according to claim 14, wherein the reaction medium is a mixture of water:alcohol with a weight ratio between the two of 99:1 to 1:99.

26. The process according to claim 25, wherein the weight ratio water:alcohol is between 90:10 and 5:95.

27. The process according to claim 14, wherein the reaction is carried out at a temperature ranging from 0 to 90°C.

28. The process according to claim 27, wherein the temperature is between 15 and 50°C.

29. The process according to claim 14, wherein the reaction is carried out at a total pressure higher than atmospheric pressure and with a molar ratio hydrogen:oxygen ranging from 1:1 to 1:100.

30. The process according to claim 29, wherein the total pressure is between 50 and 300 atmospheres and the molar ratio hydrogen:oxygen is between 1:5 and 1:50.

31. The process according to claim 14, wherein the reaction is carried out using air as oxygen source.

32. The process according to claim 14, wherein the catalyst is used in quantities ranging from  $10^{-6}$  to  $10^{-2}$  moles of metal contained in the catalyst per litre of reaction medium.

33. The process according to claim 32, wherein the catalyst is used in quantities ranging from  $10^{-4}$  to  $10^{-3}$  moles of metal contained in the catalyst per litre of reaction medium.

34. A process for the catalytic oxidation of substrates which comprises:

(a) preparing hydrogen peroxide by the reaction of hydrogen and oxygen in a solvent containing a promoter, in the presence of a catalyst consisting of a metal of group VIII supported on an activated carbon containing acid functions, being functionalized with sulfonic groups;

(b) recovering the reaction mixture containing hydrogen peroxide;

(c) putting the reaction mixture containing  $H_2O_2$  in contact with a substrate selected from olefins, aromatic hydrocarbons, ammonia and carbonyl compounds, in the presence of a catalyst based on titanium-silicalite to obtain the desired oxidated product;

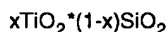
(d) recovering the oxidated product from the reaction mixture of step c); and

(e) recycling the possible non-reacted substrate in step c) and the reaction solvent in steps a) and c).

35. The process according to claim 34, wherein in step c) the catalyst is selected from titanium-silicalites with an MFI structure, titanium-silicalites with an MEL structure or intermediate MFI/MEL structure.

36. The process according to claim 35, wherein the titanium-silicalites with an MFI structure are modified with trivalent metals selected from aluminum, iron, boron or gallium.

37. The process according to claim 34, wherein the catalyst is titanium-silicalite having the formula:



wherein x represents a number between 0.0001 and 0.04.

38. The process according to claim 34, wherein said process is carried out in continuous.

## Patentansprüche

1. Katalysator, welcher für die direkte Synthese von Wasserstoffperoxid, ausgehend von Wasserstoff und Sauerstoff, verwendet werden kann, bestehend aus einem Metall, welches zur Gruppe VIII gehört und welches auf einem Trägermaterial getragen ist, wobei das Trägermaterial ein aktivierter Kohlenstoff ist, welcher Säurefunktionen enthält, welche mit Sulfongruppen funktionalisiert sind.

2. Katalysator nach Anspruch 1, worin das Metall der Gruppe VIII ausgewählt ist aus Palladium, Platin, Ruthenium, Iridium, Rhodium oder Kombinationen von diesen.

3. Katalysator nach Anspruch 2, worin das Metall Palladium ist.

4. Katalysator nach Anspruch 1, worin die Menge des Metalls, welches zur Gruppe VIII gehört, zwischen 0,05 und 5 Gew.% bezüglich des Trägermaterials beträgt.

5. Katalysator nach Anspruch 4, worin die Menge an Metall, welches zur Gruppe VIII gehört, zwischen 0,1 und 1 Gew.% bezüglich des Trägermaterials beträgt.

6. Katalysator nach Anspruch 1, worin der funktionalisierte, aktivierte Kohlenstoff von 0,1 bis 1 Gew.% Schwefel

enthält.

7. Katalysator nach Anspruch 1, hergestellt durch ein Verfahren, welches umfasst:

- 5 a) in Kontakt bringen des aktivierten Kohlenstoffs mit einem Sulfonierungsagens mit einem Gewichtsverhältnis von Sulfonierungsagens zu Kohlenstoff im Bereich von 1:20 bis 20:1 bei einer Temperatur im Bereich von 50 bis 350 °C; und
  - 10 b) Waschen des funktionalisierten, aktivierten Kohlenstoffs mit Wasser bis zur Neutralität des Waschwassers;
  - c) Behandeln der sulfonierten, aktivierten Kohle, die in Schritt b) erhalten wurde, mit einem Oxidierungsmittel bei einer Temperatur im Bereich von 30 bis 100 °C;
  - 15 d) Waschen des funktionalisierten, aktivierten Kohlenstoffs, erhalten in Schritt c), bis zum Verschwinden des Oxidierungsmittels in dem Waschwasser und Trocknen bei einer Temperatur von 100 bis 120 °C; und letztlich
  - e) Aufbringen des Metalls der Gruppe VIII auf den aktivierten Kohlenstoff, der mit den Sulfongruppen funktionalisiert ist.
- 20 8. Katalysator nach Anspruch 7, worin dem Schritt a) der Schritt a') vorangeht, worin der aktivierte Kohlenstoff mit einer wässrigen, 1 bis 10 Gew.-%igen Salzsäurelösung bei einer Temperatur von 50 bis 80 °C gewaschen wird.
- 25 9. Katalysator nach Anspruch 7, worin in Schritt a) das Gewichtsverhältnis von Sulfonierungsagens zu Kohlenstoff zwischen 1:5 und 5:1 beträgt, die Temperatur variiert von 70 bis 200 °C.
- 30 10. Katalysator nach Anspruch 7, worin das Sulfonierungsmittel ausgewählt ist aus Schwefelsäure, SO<sub>3</sub> und Oleum.
11. Katalysator nach Anspruch 7, worin in Schritt c) eine wässrige Lösung von Wasserstoffperoxid mit einer Konzentration von 1 bis 4 Gew.% verwendet wird, mit einem Gewichtsverhältnis von sulfoniertem, aktiviertem Kohlenstoff und wässriger Lösung von Wasserstoffperoxid im Bereich von 1:10 bis 1:100.
- 35 12. Katalysator nach Anspruch 11, worin das Gewichtsverhältnis von sulfoniertem, aktiviertem Kohlenstoff und wässriger Lösung an Wasserstoffperoxid zwischen 1:20 und 1:50 liegt.
- 40 13. Katalysator nach Anspruch 7, worin in Schritt c) die Temperatur zwischen 50 und 70 °C beträgt.
14. Verfahren für die direkte Herstellung von Wasserstoffperoxid mittels der Reaktion von Wasserstoff und Sauerstoff in einem Lösemittel, welches einen Promoter in Gegenwart eines Katalysators enthält, wobei der Katalysator aus einem Metall der Gruppe VIII besteht und auf einem Träger gehalten ist, worin der Träger ein aktivierter Kohlenstoff ist, welcher Säurefunktionen enthält, welche mit Sulfongruppen funktionalisiert sind.
- 45 15. Verfahren nach Anspruch 14, worin der metallische Katalysator der Gruppe VIII ausgewählt ist aus Palladium, Platin, Ruthenium, Iridium, Rhodium oder Kombinationen von diesen.
- 50 16. Verfahren nach Anspruch 15, worin das Metall Palladium ist.
17. Verfahren nach Anspruch 14, worin der Promoter eine Verbindung, welche ein Halogen enthält, ist.
18. Verfahren nach Anspruch 17, worin die Verbindung, welche ein Halogen enthält, ausgewählt ist aus der aus Wasserstoffbromsäure, Natriumbromid, Kaliumbromid, Natriumbromat oder Ammoniumbromid oder Verbindungen von Chlor, wie z.B. Natriumchlorid, Kaliumchlorid, Ammoniumchlorid.
- 55 19. Verfahren nach Anspruch 18, worin die Verbindung Wasserstoffbromsäure, Natriumbromid und Kaliumbromid ist.
20. Verfahren nach Anspruch 14, worin eine Menge an Promoter verwendet wird, so dass sich eine Konzentration des Halogenidions von mehr als 10<sup>-7</sup> mol pro Liter des Reaktionsmediums ergibt.
21. Verfahren nach Anspruch 20, worin eine Menge an Promoter verwendet wird, so dass sich eine Konzentration an

Halogenionen zwischen  $10^{-6}$  und  $10^{-4}$  mol pro Liter des Reaktionsmediums ergibt.

22. Verfahren nach Anspruch 14, worin das Reaktionsmedium ausgewählt ist aus Wasser, einem Alkohol oder einer Mischung derselben.

23. Verfahren nach Anspruch 22, worin der Alkohol ausgewählt ist aus Methanol, Ethanol, Isopropanol.

24. Verfahren nach Anspruch 23, worin der Alkohol Methanol ist.

25. Verfahren nach Anspruch 14, worin das Reaktionsmedium eine Mischung von Wasser zu Alkohol mit einem Gewichtsverhältnis zwischen den beiden von 99:1 bis 1:99 ist.

26. Verfahren nach Anspruch 25, worin das Gewichtsverhältnis Wasser:Alkohol zwischen 90:10 und 5:95 liegt.

27. Verfahren nach Anspruch 14, worin die Reaktion bei einer Temperatur im Bereich von 0 bis 90 °C ausgeführt wird.

28. Verfahren nach Anspruch 27, worin die Temperatur zwischen 15 und 50 °C beträgt.

29. Verfahren nach Anspruch 14, worin die Reaktion bei einem Gesamtdruck durchgeführt wird, der größer als atmosphärischer Druck ist mit einem molaren Verhältnis Wasserstoff:Sauerstoff im Bereich von 1:1 bis 1:100.

30. Verfahren nach Anspruch 29, worin der Gesamtdruck zwischen 50 und 300 Atmosphären und das molare Verhältnis Wasserstoff:Sauerstoff zwischen 1:5 und 1:50 beträgt.

31. Verfahren nach Anspruch 14, worin die Reaktion ausgeführt wird, indem Luft als Sauerstoffquelle verwendet wird.

32. Verfahren nach Anspruch 14, worin der Katalysator in Mengen verwendet wird im Bereich von  $10^{-6}$  bis  $10^{-2}$  mol an Metall, das in dem Katalysator enthalten ist, pro Liter des Reaktionsmediums.

33. Verfahren nach Anspruch 32, worin der Katalysator in Mengen verwendet wird im Bereich von  $10^{-4}$  bis  $10^{-3}$  mol des Metalls enthalten in dem Katalysator pro Liter Reaktionsmedium.

34. Verfahren für die katalytische Oxidation von Substraten, welches umfasst:

a) Herstellung von Wasserstoffperoxid durch die Reaktion von Wasserstoff und Sauerstoff in einem Lösemittel, welches einen Promoter enthält, in Gegenwart eines Katalysators, welcher aus einem Metall der Gruppe VIII besteht und auf einem aktivierten Kohlenstoff gehalten ist, welcher Säurefunktionen enthält, welche mit Sulfongruppen funktionalisiert sind;

b) Wiedergewinnen der Reaktionsmischung, welche Wasserstoffperoxid enthält;

c) in Kontakt bringen der Reaktionsmischung, welche  $H_2O_2$  enthält, mit einem Substrat, ausgewählt aus Olefinen, aromatischen Kohlenwasserstoffen, Ammonium- und Carbonylverbindungen in Gegenwart eines Katalysators, basierend auf Titan-Silicalit, um das gewünschte oxidierte Produkt zu erhalten;

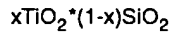
d) Wiedergewinnen des oxidierten Produktes aus der Reaktionsmischung aus von Schritt c); und

e) Zurückführen des möglichen nichtreagierten Substrats in Schritt c) und des Reaktionslösemittels in Schritt a) und c).

35. Verfahren nach Anspruch 34, worin in Schritt c) der Katalysator ausgewählt ist aus Titan-Silicaliten mit einer MFI-Struktur, Titan-Silicaliten mit einer MEL-Struktur oder MFI/MEL-Zwischen-Strukturen.

36. Verfahren nach Anspruch 35, worin die Titan-Silicalite mit einer MFI-Struktur mit einem dreiwertigen Metall modifiziert sind, welches ausgewählt ist aus Aluminium, Eisen, Bor oder Gallium.

37. Verfahren nach Anspruch 34, worin der Katalysator Titan-Silicalit mit der Formel



ist, worin x eine Zahl zwischen 0,0001 und 0,04 repräsentiert.

38. Verfahren nach Anspruch 34, worin das Verfahren kontinuierlich durchgeführt wird.

#### Revendications

1. Un catalyseur qui peut être utilisé pour la synthèse directe de peroxyde d'hydrogène en partant d'hydrogène et d'oxygène consistant en un métal appartenant au groupe VIII fixé sur un support, dans lequel ledit support est un carbone activé renfermant des fonctions acides, qui est fonctionnalisé avec des groupes sulfoniques.
2. Le catalyseur selon la revendication 1, dans lequel le métal appartenant au groupe VIII est choisi parmi le palladium, le platine, le ruthénium, l'iridium, le rhodium ou des combinaisons de ceux-ci.
3. Le catalyseur selon la revendication 2, dans lequel le métal est du palladium.
4. Le catalyseur selon la revendication 1, dans lequel la quantité de métal appartenant au groupe VIII se situe entre 0,05 et 5 % en poids par rapport au support.
5. Le catalyseur selon la revendication 4, dans lequel la quantité de métal appartenant au groupe VIII se situe entre 0,1 et 1 % en poids par rapport au support.
6. Le catalyseur selon la revendication 1, dans lequel le carbone activé fonctionnalisé renferme de 0,1 à 1 % en poids de soufre.
7. Le catalyseur selon la revendication 1, obtenu par un procédé qui comprend :
  - (a) la mise en contact du carbone activé avec un agent de sulfonation avec un rapport pondéral agent de sulfonation : carbone dans la gamme de 1 : 20 à 20 : 1, à une température dans la gamme de 50 à 350° C, et
  - (b) le lavage du carbone activé fonctionnalisé avec de l'eau jusqu'à la neutralité de l'eau de lavage ;
  - (c) le traitement du carbone activé sulfoné obtenu dans l'étape b) avec un agent oxydant, à une température dans la gamme de 30 à 100° C ;
  - (d) le lavage du carbone activé fonctionnalisé obtenu dans l'étape c) jusqu'à la disparition de l'agent oxydant dans l'eau de lavage et le séchage à une température de 100 à 120° C, et finalement
  - e) la fixation sur un support du métal du groupe VIII sur du carbone activé fonctionnalisé avec des groupes sulfoniques.
8. Le catalyseur selon la revendication 7, dans lequel l'étape a) est précédée par une étape a') dans laquelle le carbone activé est lavé avec une solution aqueuse d'acide chlorhydrique de 1 à 10 % en poids, à une température dans la gamme de 50 à 80° C.
9. Le catalyseur selon la revendication 7, dans lequel dans l'étape a) le rapport pondéral agent de sulfonation : carbone se situe entre 1 : 5 et 5 : 1, et la température varie de 70 à 200° C.
10. Le catalyseur selon la revendication 7, dans lequel l'agent de sulfonation est choisi parmi l'acide sulfurique, SO<sub>3</sub> et l'oléum.
11. Le catalyseur selon la revendication 7, dans lequel dans l'étape c), on utilise une solution aqueuse de peroxyde d'hydrogène à une concentration dans la gamme de 1 à 4 % en poids, avec un rapport pondéral carbone activé sulfoné et solution aqueuse de peroxyde d'hydrogène dans la gamme de 1 : 10 à 1 : 100.
12. Le catalyseur selon la revendication 11, dans lequel le rapport pondéral carbone activé sulfoné et solution aqueuse de peroxyde d'hydrogène se situe entre 1 : 20 et 1 : 50.
13. Le catalyseur selon la revendication 7, dans lequel dans l'étape c) la température est située entre 50 et 70° C.

14. Un procédé pour la production directe de peroxyde d'hydrogène au moyen de la réaction d'hydrogène et d'oxygène dans un solvant qui renferme un activateur en présence d'un catalyseur consistant en un métal du groupe VIII fixé sur un support, dans lequel ledit support est un carbone activé renfermant des fonctions acides, qui est fonctionnalisé avec des groupes sulfoniques.
- 5 15. Le procédé selon la revendication 14, dans lequel le catalyseur métallique du groupe VIII est choisi parmi le palladium, le platine, le ruthénium, l'iridium, le rhodium ou des combinaisons de ceux-ci.
16. Le procédé selon la revendication 15, dans lequel le métal est du palladium.
- 10 17. Le procédé selon la revendication 14, dans lequel l'activateur est un composé renfermant un halogène.
18. Le procédé selon la revendication 17, dans lequel le composé renfermant un halogène est choisi parmi le groupe comprenant l'acide bromhydrique, le bromure de sodium, le bromure de potassium, le bromate de sodium ou le bromure d'ammonium ou des composés de chlore comme le chlorure de sodium, le chlorure de potassium, le chlorure d'ammonium.
- 15 19. Le procédé selon la revendication 18, dans lequel le composé est l'acide bromhydrique, le bromure de sodium et le bromure de potassium.
- 20 20. Le procédé selon la revendication 14, dans lequel on utilise une quantité d'activateur qui est apte à donner une concentration d'ion halogénure de plus de  $10^{-7}$  moles par litre de milieu de réaction.
21. Le procédé selon la revendication 20, dans lequel on utilise une quantité d'activateur qui est apte à donner une concentration d'ion halogénure comprise entre  $10^{-6}$  et  $10^{-4}$  moles par litre de milieu de réaction.
- 25 22. Le procédé selon la revendication 14, dans lequel le milieu de réaction est choisi parmi l'eau, un alcool ou un mélange de ceux-ci.
- 30 23. Le procédé selon la revendication 22, dans lequel l'alcool est choisi parmi le méthanol, l'éthanol, l'isopropanol.
24. Le procédé selon la revendication 23, dans lequel l'alcool est le méthanol.
25. Le procédé selon la revendication 14, dans lequel le milieu de réaction est un mélange eau : alcool, avec un rapport pondéral entre les deux de 99 : 1 à 1 : 99.
- 35 26. Le procédé selon la revendication 25, dans lequel le rapport pondéral eau : alcool se situe entre 90 : 10 et 5 : 95.
27. Le procédé selon la revendication 14, dans lequel la réaction est mise en oeuvre à une température dans la gamme de 0 à 90° C.
- 40 28. Le procédé selon la revendication 27, dans lequel la température se situe entre 15 et 50° C.
29. Le procédé selon la revendication 14, dans lequel la réaction est mise en oeuvre à une pression totale supérieure à la pression atmosphérique et avec un rapport molaire hydrogène : oxygène compris dans la gamme de 1 : 1 à 1 : 100.
- 45 30. Le procédé selon la revendication 29, dans lequel la pression totale se situe entre 50 et 300 atmosphères et le rapport molaire hydrogène : oxygène se situe entre 1 : 5 et 1 : 50.
- 50 31. Le procédé selon la revendication 14, dans lequel la réaction est mise en oeuvre en utilisant de l'air comme source d'oxygène.
32. Le procédé selon la revendication 14, dans lequel le catalyseur est utilisé selon des quantités comprises dans la gamme de  $10^{-6}$  à  $10^{-2}$  moles de métal contenu dans le catalyseur par litre de milieu de réaction.
- 55 33. Le procédé selon la revendication 32, dans lequel on utilise le catalyseur selon des quantités comprises dans la gamme de  $10^{-4}$  à  $10^{-3}$  moles de métal contenu dans le catalyseur par litre de milieu de réaction.



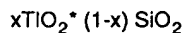
34. Un procédé pour l'oxydation catalytique de substrats qui comprend :

- (a) la préparation du peroxyde d'hydrogène par la réaction d'hydrogène et d'oxygène dans un solvant contenant un activateur, en présence d'un catalyseur consistant en un métal du groupe VIII fixé sur du carbone activé renfermant des fonctions acides, qui est fonctionnalisé avec des groupes sulfoniques ;
- (b) la récupération du mélange de réaction contenant le peroxyde d'hydrogène ;
- (c) la mise en contact du mélange de réaction contenant  $H_2O_2$  avec un substrat choisi parmi les oléfines, les hydrocarbures aromatiques, l'ammoniaque et les composés carbonyle, en présence d'un catalyseur à base de titane-silicalite pour obtenir le produit oxydé désiré ;
- (d) la récupération du produit oxydé du mélange de réaction de l'étape c) ; et
- (e) le recyclage du substrat éventuel n'ayant pas réagi dans l'étape c) et du solvant de réaction dans les étapes a) et c).

35. Le procédé selon la revendication 34, dans lequel dans l'étape c) le catalyseur est choisi parmi les titane-silicalites avec une structure MFI, les titane-silicalites avec une structure MEL ou une structure MFI/MEL intermédiaire.

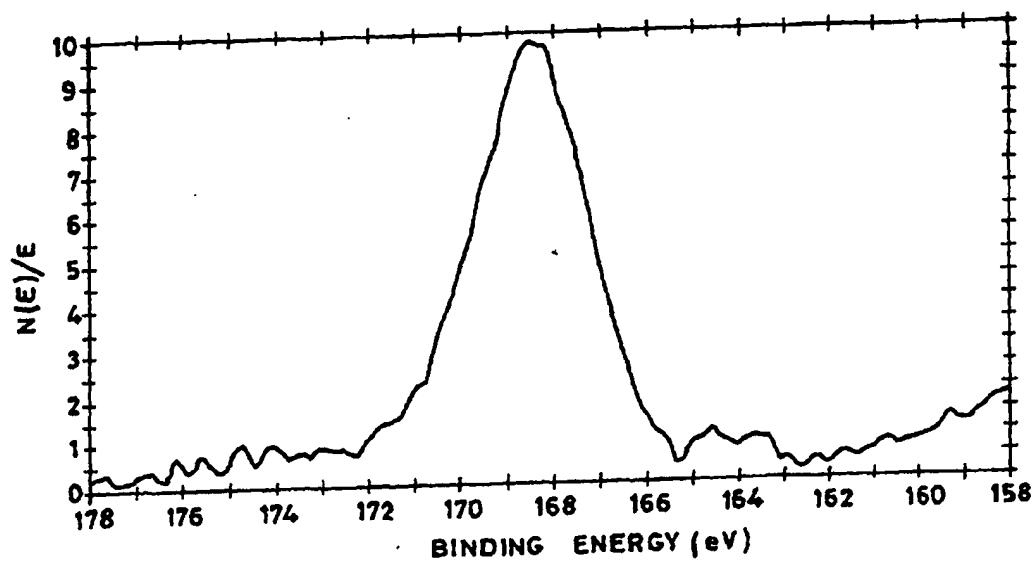
36. Le procédé selon la revendication 35, dans lequel les titane-silicalites avec une structure MFI sont modifiés avec des métaux trivalents choisis parmi l'aluminium, le fer, le bore ou le gallium.

37. Le procédé selon la revendication 34, dans lequel le catalyseur est du titane-silicalite répondant à la formule :



dans laquelle x représente un nombre compris entre 0,0001 et 0,04.

38. Le procédé selon la revendication 34, dans lequel ledit procédé est mis en oeuvre en continu.

Fig.1Fig.2